

First-principles energetics of water: a many-body analysis

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Standard forms of density-functional theory (DFT) have good predictive power for many materials, but are not yet fully satisfactory for solid, liquid and cluster forms of water. We use a many-body separation of the total energy into its 1-body, 2-body (2B) and beyond-2-body (B2B) components to analyze the deficiencies of two popular DFT approximations. We show how machine-learning methods make this analysis possible for ice structures as well as for water clusters. We find that the crucial energy balance between compact and extended geometries can be distorted by 2B and B2B errors, and that both types of first-principles error are important.

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The pioneering work of Parrinello, Car and others in the 1990s [1] initiated a major effort to understand the properties of water from first principles using density-functional theory (DFT). This effort is important not just for pure water, but for general aqueous systems, including solutions [2] and water on surfaces [3]. However, standard DFT methods often give less than satisfactory predictions for water in its liquid [4], crystalline [5, 6] and cluster forms [7–9], for reasons that are controversial. Strenuous efforts have been made to overcome the problems by adding correction terms, with a recent emphasis on correcting dispersion (see e.g. Refs [6, 10–14]). Here we show how a combination of quantum chemistry, machine learning and quantum Monte Carlo can be used to analyze the energetics of water in a variety of aggregation states. We find that DFT approximations often distort the energy balance between extended and compact structures, and that errors can arise from more than one part of the first-principles energy. Technical details of our calculations are given in the Supplemental Material [15].

Our starting point is that a model for the energetics of water is not fully satisfactory unless it gives good predictions for a range of aggregation states, and particularly: water clusters (including the dimer) in a variety of geometries, ice structures, and the liquid. By this criterion, standard DFT approximations need improvement, since their many errors include: inaccurate predictions of energies for some dimer geometries [7, 8]; wrong stability ordering of isomers of some clusters, notably the hexamer [9, 16]; incorrect relative energies of different ice structures [6]; errors of up to 30 % in the predicted density of the liquid [10, 12, 14, 18]; and substantial errors in the structure and diffusivity of the liquid [4, 10, 12–14].

Our analysis of water energetics is based on the many-body decomposition, in which the total energy $E_{\text{tot}}(1, 2, \dots, N)$ of a system of N monomers is expressed

as [19]:

$$E_{\text{tot}}(1, 2, \dots, N) = \sum_i E^{(1)}(i) + \sum_{i < j} E^{(2)}(i, j) + E^{(>2)}(1, 2, \dots, N). \quad (1)$$

Here, i is the collection of variables describing monomer i (position, orientation, internal distortion from equilibrium geometry), $E^{(1)}(i)$ the 1-body (1B) energy of monomer i , $E^{(2)}(i, j)$ the 2-body (2B) interaction energy of monomers i and j , and the beyond-2-body (B2B) energy $E^{(>2)}$ is everything not included in 1B and 2B energy. In this scheme, dispersion (non-local correlation) is mainly a 2B energy [20, 21], though it also contributes to the B2B energy [22]. Induction is usually regarded as the largest contributor to B2B, though many-body exchange-repulsion may also be significant [22].

We start with the water dimer, whose energy in any geometry can be accurately computed (within $0.1 \text{ mE}_h \simeq 2 \text{ meV} \simeq 0.05 \text{ kcal/mol}$ [23]) using the correlated quantum chemistry technique of CCSD(T) (coupled cluster single and double excitations with a perturbative treatment of triples) [24]. We take the difference $\delta E^{(2)}(\text{DFT}) \equiv E^{(2)}(\text{DFT}) - E^{(2)}(\text{CCSD(T)})$ as the error of any DFT approximation for the 2B energy of any dimer geometry. Following Refs. [8, 25], we study the errors $\delta E^{(2)}(\text{DFT})$ for thermal samples of dimer geometries randomly drawn from an m.d. simulation of the liquid, the simulation used here being done with the classical AMOEBA force field [26], as in Ref. [8]. Fig. 1 shows the 2B errors of the widely used PBE [27] and BLYP [28] approximations *versus* O-O distance for a sample of 198 dimer configurations [15], demonstrating (see also Refs. [8, 29]) that BLYP systematically underbinds for all distances and molecular orientations, while PBE performs better (but see Ref. [30]). We have shown recently [31] that machine-learning methods based on the ideas of Gaussian approximation po-

tentials (GAP) [32] can be used to represent accurately (within $0.1 mE_h \simeq 2 \text{ meV}$ or better) the 1B and 2B errors of chosen DFT approximations in water systems. We illustrate this by including in Fig. 1 the tiny residual 2B errors of GAP-corrected BLYP [15]. This gives a way of correcting almost perfectly for the 2B errors of any DFT approximation.

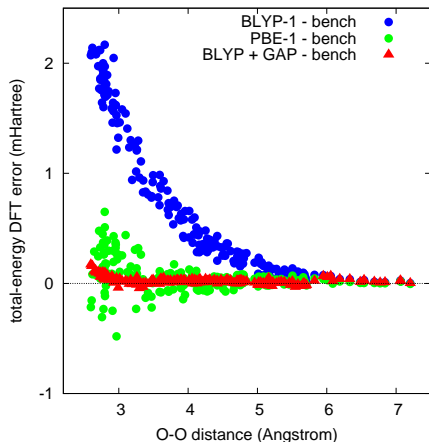


FIG. 1: Errors of 2-body energy of H_2O dimer with BLYP and PBE functionals relative to CCSD(T) benchmarks as function of O-O distance. Calculations are for sample of 198 dimer configurations drawn from a classical m.d. simulation of bulk water at ambient conditions. Also shown are residual errors of the approximation obtained by adding GAP 2-body corrections to BLYP. Units: mE_h .

The ability to correct almost exactly for 1B and 2B errors in the total energy of any water system is invaluable, because it lets us decompose DFT error into its 1B, 2B and B2B components. We show how this works for the isomers of the water hexamer. The energies of the prism, cage, book and ring isomers of the hexamer (see e.g. Ref. [9] for pictures) have been intensively studied [9, 16, 17, 33] for an important reason. For smaller clusters, the most stable isomers have ring-like geometries, but from the hexamer onwards compact geometries are more stable. Highly converged CCSD(T) calculations [33] show that the compact prism and cage are more stable than the extended book and ring isomers. However, standard DFT approximations wrongly make the extended geometries more stable [9]: our own calculations of the total energies (Fig. 2) illustrate this for PBE and BLYP [15]. If we now correct for 1B and 2B errors by adding the GAP representation of the differences $\text{DFT} - \text{CCSD(T)}$, then the errors of the resulting approximations (we denote them by PBE-2 and BLYP-2) are by definition B2B errors. As shown in Fig. 2, the errors of BLYP-2 are negative but almost constant, so that the relative energies are now excellent. The errors of PBE-2 are smaller than those of PBE itself, but are still not negligible. This means that the erroneous sta-

bility ordering with BLYP is mainly due to 2B effects, but with PBE both 2B and B2B effects are important, as pointed out in earlier work [8, 22].

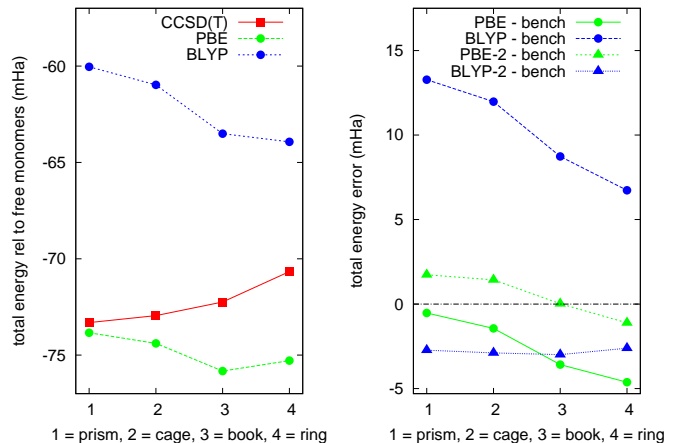


FIG. 2: Left panel: total energies of isomers of the H_2O hexamer relative to free monomers from PBE, BLYP and benchmark CCSD(T) calculations; right panel: errors of total energy of PBE and BLYP and 1- and 2-body corrected PBE-2 and BLYP-2. Units: mE_h

We turn now to the energetics of ice structures, which gives striking evidence of the difficulties of standard first-principles methods [6]. Essentially the same analysis that we used for the hexamers helps determine the nature of DFT errors for the cohesive energies of ice structures. Ice has a complicated phase diagram, with no less than 15 known crystal structures [34], but we study only the proton-ordered structures XI, II, XV and VIII forming the sequence of increasingly compact structures found at low temperatures as pressure increases from 0 to $\sim 20 \text{ kbar}$. The errors of DFT for these and other structures have recently been studied in detail [6], and it was shown that the predicted energies increase much too fast from extended to compact structures. We illustrate this in Fig. 3, where our calculated cohesive energies with PBE and BLYP [15] are compared with experimental values [35] (zero-point energies removed, see also Ref. [6]).

The GAP 1B and 2B corrections to PBE and BLYP are readily computed in periodic boundary conditions [31], and Fig. 3 shows the errors of the uncorrected and corrected approximations for the XI, II, XV and VIII structures. The picture resembles what we saw for the hexamers, with BLYP being increasingly underbinding as we go from extended to compact structures, but its corrected version BLYP-2 having almost constant negative errors, so that its relative energies are very good. By contrast, the corrected version PBE-2, while better than PBE itself, still gives substantial errors. This implies that for BLYP the problem with relative energies stems mainly from systematically underbinding 2B interaction, but that B2B errors are also important for PBE.

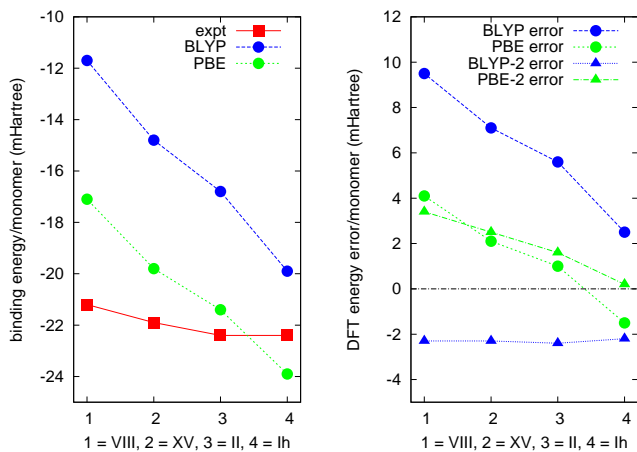


FIG. 3: Left panel: energies of ice structures relative to free monomers from PBE, BLYP and experiment; right panel: errors of PBE and BLYP and 1- and 2-body corrected PBE-2 and BLYP-2 energies. Energy units: mE_h .

The energy changes with increasing compactness along the series XI, II, XV, VIII can be understood in more detail. In all these structures, each H_2O monomer is hydrogen-bonded to four first neighbors at O-O distances of ~ 2.7 Å [34]. In XI (the proton-ordered form of the Ih structure of common ice) the monomers form a tetrahedral network, the second-neighbors being at the large distance of 4.5 Å. From XI to II, XV and VIII, the hydrogen-bonded 1st-neighbor distances change only slightly, but the 2nd-neighbor distances contract dramatically, until in VIII each monomer has eight neighbors at almost equal distances of ~ 2.8 Å, four of which are unbonded to the central monomer [34]. The close approach of monomers that are not H-bonded to each other in the compact structures appears to be implicated in the large DFT errors, as has been pointed out before (e.g. Ref. [12]).

To further probe the DFT errors in the denser ice structures, we cut from ice VIII the nonamer composed of an H_2O molecule and its nearest neighbors, and we study the energy changes when the H-bonded neighbors are held fixed but the unbonded neighbors are moved radially. We calculated benchmark energies for the resulting configurations using diffusion Monte Carlo [15, 36], which is extremely accurate both for water clusters and for ice structures [6, 8, 9], including ice VIII. Comparison with PBE and BLYP energies [15] (Fig. 4) shows that both approximations give excessive energy increases on going from extended to compact configurations. Comparing the GAP-corrected approximations PBE-2 and BLYP-2 with uncorrected PBE and BLYP (Fig. 4), we see again what we learnt from the hexamers and the ice structures. Correction for 1B and 2B errors takes BLYP from severely underbinding to somewhat overbinding, but with almost constant B2B errors; corrected PBE, while better than uncorrected PBE, still suffers from similar (though

smaller) errors, so that B2B effects are important.

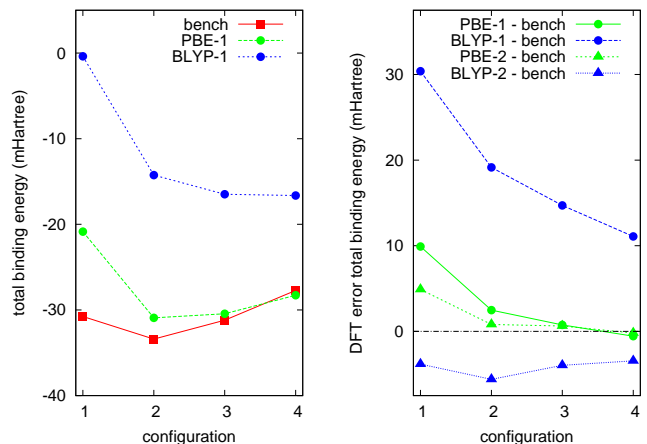


FIG. 4: Left panel: total binding energies of the four nonamers derived from the ice VIII structure computed with DMC, PBE-1 and BLYP-1; non-bonded neighbors move radially outward as we go from left to right. Right panel: errors of the total energy relative to DMC with PBE-1, BLYP-1, PBE-2 and BLYP-2 DFT approximations. Energy units: mE_h .

Several key points emerge from our analysis. First, the pervasive importance of the energy balance between extended and compact structures is highlighted by the fact that we see the same pattern of DFT errors in the hexamers, the ice structures and the nonamer configurations. Second, we have seen that both 2B and B2B errors can distort this balance. With the BLYP functional, 2B errors are the main culprit in tipping the balance towards extended structures, but with PBE the contribution of B2B errors is significant. Third, it is clear that different kinds of B2B errors are important. With PBE, the B2B errors appear to be associated with the close approach of monomers that are not H-bonded to each other (ice structures, nonamer) or that involve highly distorted H-bonds (hexamers). With BLYP, by contrast, B2B overbinding occurs even for extended structures, and may be due to exaggerated cooperativity of H-bonding. Since dispersion is expected to be mainly a 2B interaction in water, our results clearly indicate that sources of error in addition to the poor treatment of dispersion should be considered.

Is our analysis relevant to the first-principles understanding of the density, structure and diffusivity of liquid water? It seems likely that the systematic 2B underbinding of BLYP accounts both for its under-prediction of the equilibrium density and for its prediction of an over-structured and under-diffusive liquid; however, its B2B overbinding might also be expected to contribute to over-structuring and under-diffusivity. On the other hand, the under-prediction of the density by PBE may arise from the excessive 2B and B2B repulsion involving H_2O monomers that are not H-bonded to each other, an effect that could also account for over-structuring and under-

diffusivity. These suggestions may be directly testable, since diffusion Monte Carlo should be able to provide accurate total-energy benchmarks for the liquid in periodic boundary conditions; if so, the many-body analysis given here would be feasible for thermal samples of the liquid.

Our analysis of first-principles errors for a variety of water systems into 1-, 2- and beyond-2-body components gives helpful insights into their fundamental energetics, but a detailed energy decomposition analysis (see e.g. Ref. [22]) is also needed, including an assessment of the role of non-local electron correlation in the energetics of the dimer and the other water systems studied here.

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